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gone on to make comparison with allied European forms as beautifully figured in Meyer and Möbius' "Fauna der Kielerbucht" and elsewhere, but he has stopped with a bare record of facts from which he leaves others to extract the conclusions.

The feature of the paper which will excite the most comment, though the least worthy of it, is the savage onslaught on present-day nomenclatorial methods, backed up by the deliberate retention of the nomenclature of fifty years ago as seen in the classic "Binney's Gould." Since the author expressly states that he follows this particular work consistently, and since that work is so important that its names are included in the synonymy of almost every modern list, no actual doubts can arise from this course. It will be easier for any student hereafter to ascertain the correct name of any of Morse's forms that it would have been if, for instance, he had used the 1915 nomenclature when he ought to have followed the fashion of 1919. Particularly is this true as to the generic names, but it does seem a pity not to use a certain discrimination as to specific names. For instance, to call Gould's "*Modiolaria discors*" a "*Modiolaria*" can cause no doubt or confusion even though "*Modiolaria*" has suffered a recent dislocation very likely temporary. But to call it "*discors*" when it is really *substriata* Gray and widely distinct from the strictly European *discors* for which Gould mistook it, is to perpetuate a demonstrated error of fact.

As for the slashing attack on modern nomenclatorial vagaries it probably will have small effect; first because it covers a field already well debated and second because the criticism is almost entirely destructive. It may fairly be said that Professor Morse is as much at fault for failing to recognize that the old system had become nearly intolerable as the perpetrators of the new system are for failing to recognize that it is equally nearly intolerable if not more so. It may serve a useful purpose if it helps awaken the conscientious and learned but timid and unimaginative men who have made a mess of modern nomenclature to the fact that while

they are repelling young students and driving them to other fields on the one hand, they are disgusting and irritating old masters to the point of open rebellion on the other.

The paper contains altogether too many typographical errors; and a few slips on the author's part—as where he says (p. 167) that besides *Glycimeris siliqua* the only other form he is acquainted with having the anal siphon larger than the branchial is *Anatina papyracea* and then (p. 190) both figures and describes *Ceronia arctata* as showing the same condition.

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SPECIAL ARTICLES

RESEMBLANCES BETWEEN THE PROPERTIES OF SURFACE-FILMS IN PASSIVE METALS AND IN LIVING PROTOPLASM, II.

ACTION OF SALT SOLUTIONS AND ORGANIC COMPOUNDS. ANTAGONISMS

PURE solutions of the majority of neutral salts activate passive iron, at a rate which varies with the nature and concentration of the salt. Both classes of ions are concerned in the effect.

In general the stability of the surface-film in any solution—and hence the preservation of the passive state—is intimately dependent upon the oxidizing properties of the dissolved substances. Many solutions whose oxidizing power is insufficient to impart passivity to active iron retard or prevent the spontaneous return of the passive metal to the active state; this is true, *e. g.*, of weak solutions of nitric acid or bichromate ($m/10$ to $m/50$). Obviously when a solution imparts passivity it also preserves it, but the reverse is not always true. In media with no definite oxidizing action, *e. g.*, distilled water, passivity soon disappears; continued oxidation seems necessary for its preservation.

The following experiments have aimed at a more precise determination of the conditions under which the passive state is preserved or destroyed in different solutions; evidently such conditions correspond to the conditions of stability of the surface-film. Iron wires

were first passivated by exposure to 1.42 HNO_3 ; they were then washed thoroughly in distilled water¹ and transferred to the solution under examination; after the lapse of a measured time of exposure they were again washed in water and placed in dilute HNO_3 (*s. g.*, 1.20). If activation has occurred in the solution, darkening of the surface and effervescence begin instantly; while if the exposure has been insufficient, no effect is seen and the wire remains passive.

In most solutions of salts and other electrolytes a spontaneous return of activity occurs after a greater or less interval, the length of which depends upon the nature and concentration of the compound. In the total effect produced by the solution both classes of ions are concerned; and no relation of activating or passivating influence to the sign of ionic charge is apparent. All ions of strong oxidizing properties tend to stabilize the passive condition (*e. g.*, Cr_2O_7 , MnO_4 , Ag, Au, Pt), while others (especially Cl, Br, I) have a strong activating influence, referable possibly to a colloidal (aggregative or dispersive) action upon the film. In pure solutions of alkali and alkali earth salts (except those with strongly oxidizing anions like MnO_4 and Cr_2O_7) passivity is always soon destroyed, within periods ranging from a few seconds or minutes to half an hour or sometimes longer. The presence of oxygen in the anion (especially if in a terminal position) appears always to retard the process of activation. In solutions of nitrates, chlorates, phosphates, sulphates, carbonates, tartrates, citrates, acetates ($m/2$ to $m/20$) passivity remains for usually several minutes; activation is more rapid with hydrates; while halides in much lower concentration activate within a few seconds.

Different specimens of iron vary considerably in the time required for activation in a

¹ Passive wires retain their passivity in distilled water for a considerable period—ranging in various experiments from 15 to 23 minutes at room temperature—but not indefinitely, a fact again indicating that the passive state is preserved only when there is the possibility of continued rapid oxidation.

given solution, apparently because of variations in the finer structure of the metal. All of the following observations were made with the same kind of wire (no. 20 piano wire, *ca.* 1 mm. in diameter); the metal of this wire is, however, not homogeneous; in particular it was always found that freshly cut and slightly used wires were decidedly more sensitive to activation than wires which had been used for some time and in which the outer layer had been dissolved away. Apparently the surface-layer of a drawn wire is less homogeneous than the core, and hence forms a less uniform and stable passivating surface-film. To obviate this source of irregularity, in the following experiments wires were used which had been reduced by the acid to two thirds or less of the original diameter. Such wires when passivated exhibit a relatively uniform behavior in salt solutions, although in the more slowly activating solutions the exact time required for activation still shows considerable variation. This variability has probably the same basis as the variability in the rusting properties of different specimens of iron. In each trial of a particular solution in any series of experiments several independent determinations with different wires are therefore necessary; as a rule these show good agreement, with occasional well-marked variations, due presumably to accidental variations of structure or composition in the exposed surface of the metal.

Halides.—Solutions of metallic chlorides, including those of noble metals (Hg, Au, Pt), activate passive iron with great rapidity. The following series of experiments with four chlorides are typical and illustrate the dependence of time of activation upon concentration; they also show the relative unimportance of the cation in such solutions. In each solution seven trials with seven separate wires were made with each length of exposure; time was marked by a metronome; the wires were transferred by glass hooks from the distilled water to the tubes containing the solutions. The time given is the usual minimal exposure required to render the passive wire reactive to dilute HNO_3 ; with briefer exposures the wires remain passive.

Conc.	NaCl	KCl	CaCl ₂	HCl
<i>m</i> /50	ca. 1 sec.	ca. 1 sec.	ca. 1 sec.	ca. 1 sec.
<i>m</i> /100	1 to 2 "	1 to 2 "	ca. 1 "	1 to 2 "
<i>m</i> /200	3 "	ca. 3 "		
<i>m</i> /400	4 to 5 "	ca. 5 "	2 "	4 to 5 "
<i>m</i> /800	ca. 6 "	10 "	4 to 5 "	
<i>m</i> /1,000				10 to 12 "
<i>m</i> /1,200	ca. 10 "		ca. 8 "	
<i>m</i> /1,600		16 "		

These series were carried out at different times and with different wires, and the results are not strictly comparable. In general, however, the rate of the activating process, in the case of each salt, is approximately proportional to the concentration. A progressive alteration of the surface-film, at a rate determined by the concentration of Cl⁻ ions, appears to underlie the effect. With the above chlorides the nature of the cation seems indifferent; but with the chlorides of noble metals a retarding influence of the cation is apparent; thus *m*/4 HgCl₂ required 2 to 3 seconds for activation and *m*/8 HgCl₂ 3 to 4 seconds. A comparison of the three chief halides showed a decreasing velocity of activation in the order, Cl, Br, I; in *m*/50 solution the minimal times for activation were: NaCl, 1 to 2 seconds; NaBr, 3 to 4 seconds; NaI, 12 to 14 seconds.

Other Salts.—Activation occurs much more gradually in solutions of other salts. The following results are typical for the minimal activating exposures in *m*/2 solutions of sodium salts:

NaOH	10 to 30 seconds
Na ₂ CO ₃	2 to 4 minutes
Na ₂ SO ₄	1 to 10 minutes
Na ₂ HPO ₄	3 to 5 minutes
Na-acetate	30 sec. to 4 min.
Na-tartrate	2 to 4 minutes
Na-citrate	5 to 10 minutes
NaNO ₃	5 to 20 minutes
NaClO ₃	2 to 30 minutes
NaCN	5 to 7 minutes

The figures given represent the extremes of different observations with wires of varying sensitivity. Passivity is preserved longest in solutions of nitrates and chlorates, but all salts with terminal oxygen in the anion

activate slowly. Why cyanide should act similarly is difficult to say; the whole subject should be investigated thoroughly. It is noteworthy that in nitrate solutions no definite relation between concentration and velocity of activation was found; in all of the solutions examined activity appeared only after the lapse of several minutes; and apparently its precise moment of appearance depends largely on casual conditions, especially irregularities in the structure of the metal. The following list gives the minimal times of exposure observed in a series of solutions of NaNO₃.

Conc.	Active after
<i>m</i>	10 minutes
<i>m</i> /2	4 "
<i>m</i> /4	8 "
<i>m</i> /8	> 10 "
<i>m</i> /16	10 "
<i>m</i> /32	6 "
<i>m</i> /64	6½ "
<i>m</i> /128	4 "
<i>m</i> /256	> 8 "
<i>m</i> /512	6 "

In this series the least effective exposure was 4 minutes, and there was no apparent relation to concentration. Not infrequently wires have been found passive after 15 or 20 minutes in solutions of NaNO₃. In all probability the structural conditions at the surface of the metal, which in such experiments are determined by casual conditions beyond control, are a main factor determining the precise rate of activation in any instance. An analogy is offered by the case of rusting, the rate of which depends not so much upon the concentration of oxygen and the conductivity of the solution as upon the special character of the metal; this determines the number of local couples to whose electrolytic action the chemical change is chiefly due. Pure and homogeneous specimens of iron rust very slowly, even under the most favorable conditions.¹

In the above solutions the delay in activa-

¹ Cf. Walker, Cederholm and Bent, *Jour. Amer. Chem. Soc.*, 1907, Vol. 29, p. 1251; Lambert, *Jour. Chem. Soc.*, 1910, Vol. 97, *Trans.*, p. 2426, and 1912, Vol. 101, p. 2056; Dunstan and Hill, *ibid.*, 1912, Vol. 99, p. 1835.

tion depends upon the oxidizing properties of the anion. In solutions of alkali salts with anions of still greater oxidizing power, *e. g.*, bichromates and permanganates, passivity is preserved indefinitely. These salts, as well known, are strong passivating agents; a saturated solution of KMnO_4 passivates active iron wires with one or two seconds exposure or even less.

The nature of the cation is also an important factor in the activating or passivating action of a salt. Passive wires retain their passivity longer in solutions of heavy metal salts (especially nitrates) than in corresponding solutions of alkali and alkali earth salts. This is well illustrated by copper salts; in $m/20 \text{ CuCl}_2$ activation is rapid (1 to 2 seconds), as in all solutions of chlorides; in $m/20 \text{ CuSO}_4$ it usually requires from 5 to 10 minutes, and in $m/20 \text{ Cu}(\text{NO}_3)_2$ more than 30 minutes. A similar relation is seen with acids; $m/10 \text{ HCl}$ activates in less than 1 second; $m/10 \text{ H}_2\text{SO}_4$ requires several minutes; while in $m/10 \text{ HNO}_3$ passivity is preserved indefinitely. The nitrates of metals with a lower solution-tension than passive iron (AgNO_3 , $\text{Hg}(\text{NO}_3)_2$) also preserve passivity indefinitely and their solutions act as strong passivating agents.

In solutions of copper salts the precise activation-time can be measured with accuracy in a single wire if the wire is kept under close observation, for at the moment when activation is complete metallic copper begins to be deposited upon the bright surface of the iron and in a few seconds the original steel-white luster changes to a dull copper-red. A large number of observations have been made on the influence of different conditions (especially presence of organic compounds, oxidizing agents, and salts of noble metals) upon the rate of activation in $m/20 \text{ CuSO}_4$ and $\text{Cu}(\text{NO}_3)_2$; in such mixed solutions antagonism-effects are well-marked and will be described below.

An interesting feature in the behavior of passive wires in these solutions is that activation (involving as it does the deposition of copper on the iron surface) has a marked influence upon the subsequent behavior of the

same wire when it is repassivated and returned to the same solution. Unless the copper coating is removed very completely from such a wire before repassivation, the latter is always found to be distinctly more reactive in the copper salt solution than before, *i. e.*, activation occurs in a much shorter time. My usual procedure in repassivating wires after activation in solutions of copper salts has been to dissolve off the adhering copper with dilute HNO_3 and then wipe the wire carefully with a coarse cloth until everywhere bright and clean before placing in strong HNO_3 for repassivation. But if the copper is imperfectly removed before repassivation (*e. g.*, by simply rubbing the wire with the cloth), and especially if the stay in strong acid is brief, the wire is typically found to become active in the salt-solution within a briefer period than normally. Thus with wires carefully cleaned before passivation, the average time of activation in $m/20 \text{ CuSO}_4$, with 36 trials with different wires, was 11 minutes; while with wires which were passivated with some copper still adhering the average of 31 trials was 3 minutes. In $m/20 \text{ Cu}(\text{NO}_3)_2$ the respective times were: carefully cleaned wires, 34.2 minutes; imperfectly cleaned wires, 19.7 minutes (average of 20 trials in each case). Although the two sets of wires have the typical steel luster after passivation and are then indistinguishable in appearance, it is probable that the sensitizing effect of the previous activation is to be referred to the presence of minute particles of copper which remain adhering to the surface of the iron and by acting as anodal regions or nuclei exert upon the general film-covered surface an influence favorable to activation. Under normal conditions the contact of metallic copper activates passive iron; presumably, therefore, the presence of this adhering copper would have the same influence in promoting activation as the simultaneous contact of numerous particles of the metal at different points of the surface; the activation-process is facilitated and occupies a shorter time than before. Activation in a solution of a copper salt thus renders the metal for a time more sensitive to a second

activation—a condition which has many general biological analogies and suggests that the basis for many phenomena of sensitization and memory in organisms may consist in a deposition of specific materials in the surface-films of the sensitive elements. In other words, some specific and lasting change in composition is the direct result of the response to stimulation, and increases the sensitivity to a subsequent stimulation of the same kind.

Antagonisms.—In general any condition that confers increased stability upon the surface-film prevents or retards its destruction in an activating solution and hence preserves passivity. Accordingly strongly oxidizing compounds like peroxides, bichromates, permanganates, osmium tetroxide, salts of noble metals (Hg, Ag, Au, Pt) antagonize the activating effects of sodium nitrate and other salt solutions upon passive iron. The addition of one mol of AgNO_3 to 100 mols of NaNO_3 in a solution of the latter salt entirely prevents spontaneous activation. The antagonism between Na and Ca salts, however, which is so characteristic of biological systems, is not exhibited by passive iron, or only slightly. It is also difficult to antagonize the activating effect of chlorides; for example, in $m/60$ NaCl the addition of $\text{K}_2\text{Cr}_2\text{O}_7$ to a total concentration of 0.08 m. was found to preserve passivity indefinitely, but 0.04 m. proved insufficient, although it prolonged the time of activation from one or two seconds (the time in pure $m/60$ NaCl) to about 30 seconds.

The activating influence of the Cl -ion is thus counteracted only by a great excess of the oxidizing agent. A less strongly oxidizing salt like NaNO_3 has only a slight antagonizing effect with chlorides; thus in a series of mixtures of $m/50$ NaCl and $m/50$ NaNO_3 in all proportions, using passive wires which underwent activation in pure $m/50$ NaCl in 2 to 3 seconds, the activation-time was prolonged to only 7 or 8 seconds in a solution containing 1 part NaCl to 4 parts NaNO_3 , and to 20 or 25 seconds in a solution of 1 part NaCl to 9 parts NaNO_3 . In the pure $m/50$ NaNO_3 activation requires five minutes or more. The prepotent action of the Cl -ion is thus evident.

The action of AgNO_3 in solutions of sodium nitrate, chlorate, sulphate or acetate affords a typical instance of ion-antagonism in which the protective effect is due to the cation of the added salt. Many biological antagonisms are of this class. The following brief summary of typical experiments will illustrate. Passive wires were placed in solutions of the four sodium salts named, both pure and with the addition of AgNO_3 as indicated.

Solution		Result
Pure	$m/10$ NaNO_3 , NaClO_3 , Na_2SO_4 , or NaCOOCH_3	Wires are all active within 30 minutes or less.
99 vols. $m/10$ <i>plus</i> 1 vol. $m/10$	Na-salt AgNO_3	Wires in NaNO_3 , NaSO_4 and NaCOOCH_3 re- mained passive indefi- nitely; in NaClO_3 they became active in respectively 1 hour, 2½ hours, and 50 minutes in three successive trials.
98, 97 96 and 95 vols. $m/10$	Na-salt <i>plus</i>	All wires remained pas- sive indefinitely. (respectively) 2, 3, 4 and 5 vols. $m/10$ AgNO_3 .

Salts of other noble metals (Hg, Au, Pt) similarly prevent spontaneous activation in solutions of NaNO_3 . Of the two mercuric salts, chloride and nitrate, the former proved ineffective in the three mixed solutions used, viz., 95, 90 and 80 vols. $m/10$ NaNO_3 *plus* (respectively) 5, 10 and 20 vols. $m/10$ HgCl_2 ; in these solutions the action of the Cl -ions overbalances that of the Hg -ions; but in corresponding solutions containing $\text{Hg}(\text{NO}_3)_2$ instead of HgCl_2 passivity was preserved indefinitely. Similarly a slight addition of AuCl_3 or PtCl_4 to $m/10$ NaNO_3 prevented spontaneous activation and preserved passivity indefinitely (*e. g.*, 2 or 4 c.c. of a 1 per cent. solution of either salt to 100 c.c. of $m/10$ NaNO_3).

It is significant that such salts exhibit protective action only if the metal is nobler than passive iron; similar addition of $\text{Ca}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ to $m/10$ NaNO_3 had no such effect. Apparently the metal of the

antagonizing salt must be of such a nature that its contact (as metal) with passive iron promotes passivity rather than activity; thus it is well known that contact of passive iron with copper, lead and other baser metals causes activation, while contact with mercury and the nobler metals has no such effect and indeed promotes passivity. Hence any metallic particles of the former class which may be deposited on the iron surface serve as activating centers (*i. e.*, are anodic relatively to passive iron), while those of the latter class have a reverse or passivating influence. The ability of any cation to prevent activation thus depends upon the electrical potential of the metal in relation to that of the passive iron surface. In other words, the passivating effect is a direct function of the oxidizing potential of the ion in question, *i. e.*, the readiness with which it parts with its positive charge (or receives electrons).

As already shown, the activating effect of the NaNO_3 solution is equally well prevented by the addition of small quantities of salts with strongly oxidizing anions, like $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 ; oxidizing non-electrolytes like H_2O_2 and OsO_4 have a similar influence. Ionic antagonism is thus not a function of the sign of the ionic charge, but of the special chemical—more specifically oxidizing—properties of the ion. Non-electrolytes with similar chemical properties are equally effective. All of these phenomena have parallels in the behavior of living systems.

Pure solutions of AgNO_3 , $\text{Hg}(\text{NO}_3)_2$, $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 both preserve passivity and have a rapid passivating action on active iron. An exposure of two or three seconds to $m/20$ AgNO_3 or $\text{Hg}(\text{NO}_3)_2$ is sufficient to confer passivity upon an active wire. The velocity of the passivation-process is high; in a series of experiments with solutions of AgNO_3 ($m/10$, $m/20$, $m/40$, $m/80$, $m/160$) it was found that even in the $m/160$ solution an exposure of three seconds was usually sufficient for passivation. Saturated KMnO_4 passivates with exposures of one second or less; $\text{K}_2\text{Cr}_2\text{O}_7$ is somewhat slower in its action.

The essential results of experiments with

surface-active organic compounds (anæsthetics) can be summarized briefly. $m/20$ CuSO_4 was used, containing in solution the compound under examination; the rate of activation was compared with that observed in the pure $m/20$ CuSO_4 . In general such compounds, unless of a definitely oxidizing chemical character (*e. g.*, nitro compounds or nitrate esters), exhibited little or no effect in either retarding or accelerating activation. The higher aliphatic alcohols, however (n-hexyl, n-heptyl, n-octyl, capryl), had a moderate retarding influence in saturated solution, an effect probably dependent on the viscosity of the adsorbed layer and the lowered electrical conductivity; little effect was found with the lower members of the series. Chloroform, ethyl ether, carbon tetrachloride, ethyl and phenyl urethanes, fatty acid esters (ethyl acetate, propionate and butyrate), chloroform, paraldehyde, chloral hydrate, benzol, naphthalene, phenanthrene, all showed little or no retarding action. On the other hand, ethyl nitrate had a well marked antagonistic effect, in one case prolonging passivity for more than twenty-four hours; nitromethane and acetone-trile also caused distinct retardation. Parallels with the general pharmacological action of the above compounds are thus not apparent in these experiments, but the existence of such parallels is perhaps hardly to be expected. In the living cell the characteristic action of these compounds appears to depend largely upon solution in the organic solvents of the protoplasm, especially the lipoids; the stability of the protoplasmic film is correspondingly altered, being increased at the anæsthetizing concentrations of the compounds. In the metal no such process of solution can occur, and whatever influence is exerted appears to depend upon the physical properties of the adsorbed layer or upon the direct chemical action of the compound upon the metal.

RALPH S. LILLIE

PHILADELPHIA MEETING OF THE AMERICAN CHEMICAL SOCIETY

THE general description of the meeting held September 2 to 6, 1919, has already been printed